

Separation of MeOH/MTBE mixtures through chitosan composite membranes using pervaporation

DongJin Woo, SangYong Nam, YoungMoo Lee

Department of Industrial Chemistry, College of Engineering,
Hanyang University, Seoul, Korea 133-791

Introduction

Chitin, which is obtained mainly from the cuticle of a marine crustacean, has recently aroused great interest in its industrial and biomedical applications. Chitosan, deacetylated form of chitin, appears to be more useful for biomedical application and dehydration of aqueous solutions than chitin, since it has both hydroxyl and amino groups that can be modified easily. Amino groups on chitosan reacts with dialdehyde to form a Schiff base and then crosslinked, and can be easily neutralized with sulfuric acid and metal ions. Polyfunctional metal ions can form a metal-polyelectrolyte complexes with chitosan.

Membranes used in modules so far working in industrial pervaporation plants are generally of composite type. This composite membrane was prepared by coating a porous polysulfone ultrafiltration membrane support of definite structure with a thin, dense layer of permselective chitosan. To apply industrial scale pervaporation process for dehydration of aqueous ethanol and isopropanol, chitosan composite membranes were prepared and tested at various conditions.

Experimental

Chitosan, a natural polymer deacetylated from chitin was purchased from Tokyo Kasei. Chitosan has a 76% deacetylation degree measured by titration method, and 500,000 molecular weight calculated by Mark-Howink equation. Glutaraldehyde, glyoxal, terephthalaldehyde and sulfuric acid is used as a crosslinking agent to crosslink the surface of composite membranes.

Chitosan composite membranes were prepared by casting chitosan solution onto porous polysulfone ultrafiltration membrane. Composite membranes to

separate water from aqueous ethanol solution were chemically and ionically crosslinked by using various crosslinking agents, dialdehyde (glutaraldehyde, glyoxal, terephthalaldehyde) and sulfuric acid.

The morphology of surface crosslinked chitosan composite membranes were examined by scanning electron microscopy. ATR-FT-IR spectra were employed to confirm the crosslinking mechanism of surface crosslinked chitosan composite membranes. X-ray diffraction patterns were performed on the Rigaku Denki RAD-C X-ray diffractometer.

Pervaporation was performed to separate water from aqueous alcohol solution and MeOH from MTBE.

Results and discussion

SEM microscopy of chitosan composite membranes is presented in Fig. 1. The morphology of the polysulfone layer has a typical finger like structure. There is no pore in active chitosan layer, and thickness of active chitosan layer less than $5\ \mu\text{m}$.

The characterization of crosslinked chitosan composite membrane by ATR-FT-IR was studied for understanding crosslinking mechanism. In the case of sulfuric acid crosslinking system, amide peaks observed in 1670 and 1550 wavenumbers were shift to 1610 and 1500 wavenumbers. This means that crosslinking by sulfuric acid was done by ionic bonding between neutralized form of amine salt in chitosan chains and sulfuric acid. When using the glutaraldehyde as a chemical crosslinking agent, concentration of glutaraldehyde, crosslinking time and annealing affected crosslinking of chitosan chains and pervaporation performances.

For both of dehydration of water/alcohol and separation of MeOH/MTBE using pervaporation, ionically crosslinked chitosan composite membrane was useful. When the chitosan composite membrane was applied to dehydration of ethanol, separation factor was about 250, and flux was $250\text{g/m}^2\text{hr}$. For isopropanol, the water concentration of permeate was above 95%, flux was above

1,500 g/m²hr. For MeOH/MTBE separation, when the feed contains 25% MeOH in the mixture, measured at 25°C, the permeate flux was about 450g/m²hr with separation factor of about 150. Further results on MeOH/MTBE separation are reported in this study.

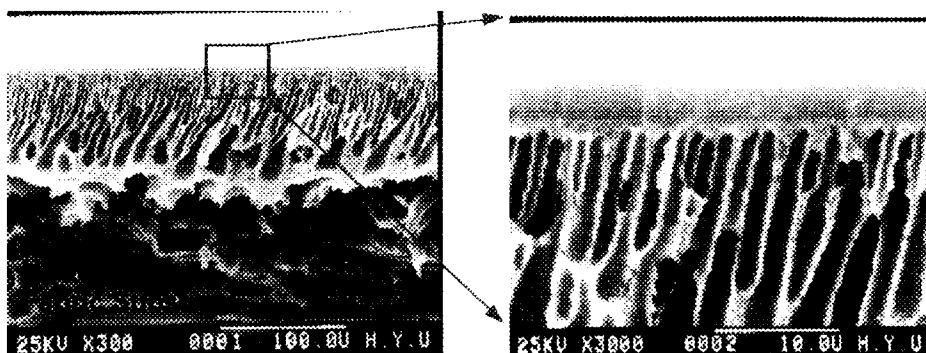


Fig 1 SEM microscopy of chitosan composite membranes

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